

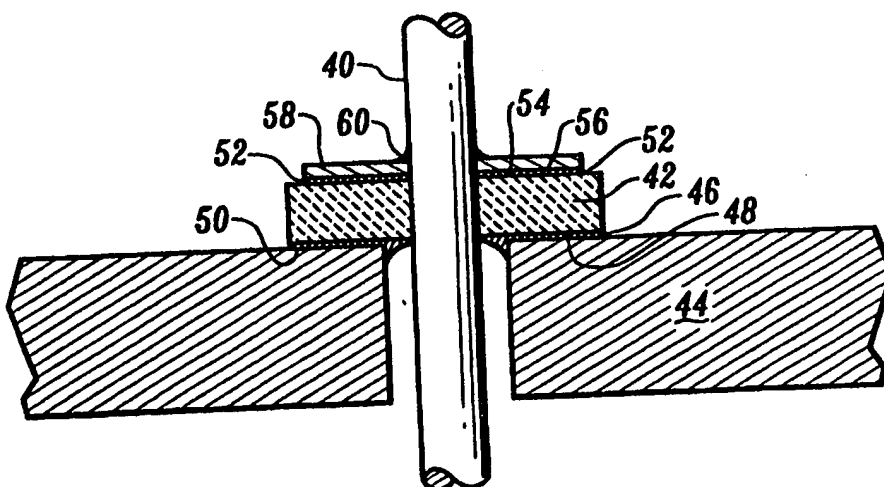
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Olds Station Road, Wenatchee, WA 98801 (US).**(72) Inventor:** LASATER, Brian, J.; 2465 Highland View Drive.
East Wenatchee, WA 98802 (US).**(74) Agents:** SPECKMAN, Ann, W. et al.; Law Offices of Ann W.
Speckman, Suite 4185, 2601 Elliott Avenue, Seattle, WA
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SN, TD, TG).**Published***With international search report.***(54) Title:** METHODS AND MATERIALS FOR SEALING CERAMIC TO METALLIC SURFACES**(57) Abstract**

Methods for sealing an interface surface of ceramic materials (42), such as zirconia, to an interface of metallic materials (40), such as titanium-containing materials, using a titanium-nickel brazes (46) are disclosed. Preferred ceramic include stabilized zirconia materials; preferred metallic include titanium-niobium alloys; and a preferred titanium-nickel braze material is a 50-50 titanium-nickel alloy. Braze materials comprising titanium, nickel, and niobium are used for joining ceramic materials to metallic materials lacking niobium. At least one of the

interfaces is contacted by the titanium-nickel braze and sealing is accomplished under vacuum conditions at temperatures from 900 to 1200 °C during application of pressure to the joint. The methods are suitable in hermetically sealing applications in implantable medical devices, electrical connectors, electronic packages, sporting goods, structural components.



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5 METHODS AND MATERIALS FOR SEALING CERAMIC TO METALLIC SURFACES

Field of the Invention

10 The present invention relates to methods and braze materials for sealing ceramic materials, such as zirconia, to metallic materials, such as titanium-containing materials, using a filler material composed of titanium and nickel and, optionally, niobium. The methods and braze materials are especially suitable for use in hermetically sealing ceramic and metallic components for applications such as implantable medical devices, electrical connectors, electronics packages, structural
15 components, and the like.

Background of the Invention

20 The development of advanced materials has accelerated in recent years. Materials of various types have properties that are desirable for a wide range of applications in diverse environments. Although the materials are highly advanced, it is often difficult to adapt them for use in applications in which they interface with materials having different properties. Sealing of dissimilar materials at interface surfaces between the materials, for example, has frequently been problematic.

25 Many applications require materials to be sealed hermetically. Providing reliable hermetic seals at the interface surfaces of materials having different properties, particularly different coefficients of thermal expansion, has been difficult. U.S. Patents 5,298,683, 5,433,260, 5,675,122, 5,110,307, 5,041,019, 5,109,594 and 4,690,480 disclose various methods for hermetically sealing different types of materials, particularly materials having different thermal properties, to one another.
30 Many of these patents relate to hermetically sealing various materials for use in electrical connectors and electronics packages using a transition joint or bushing.

35 U.S. Patent 4,991,582 discloses a sealed ceramic and metal package for electronic devices implantable in living bodies. This patent describes a device in which a ceramic sleeve is sealed to a metallic band having substantially the same coefficient of linear thermal expansion. The sleeve is formed of an inert ceramic material such as alumina or boron nitride, and the metal band is formed of niobium,

5 molybdenum or tantalum. A header plate carrying a substrate on which the electronic components are mounted and having a plurality of electrical connectors is then sealed to the metal band. The ceramic sleeve is sealed to the metal band employing a butt brazing technique using an alloy of 71.5% titanium and 28.5% nickel. Brazing is accomplished by heating the ceramic sleeve, fitted with the metal band and an annular
10 foil of brazing material. The electronic components that are ultimately mounted in the ceramic sleeve cannot tolerate the high temperatures required during the brazing operation, and are inserted into the cavity formed by the ceramic sleeve when the header is joined to the metallic band. The metal to metal seal between the header and the metal band is provided using high temperature welding, such as laser or electron
15 beam welding, having a low heat-affected zone that does not affect the integrity of the electronic components.

U.S. Patent 3,594,895 discloses 50-50 brazing alloys of titanium with iron, cobalt, nickel or mixtures thereof for sealing ceramic to metallic materials, such as tantalum, niobium and group VIII metals. The 50-50 titanium-nickel brazing alloy
20 had a melting point of 1250°C, requiring heating to temperatures just above 1250° C for brazing. The brazing process, including the heating, melting and cooling process, took about five minutes.

U.S. Patent 4,957,236 discloses a brazing alloy-filler metal for joining titanium-aluminum-niobium alloys, the filler metal comprising 37-75% titanium,
25 5-43% niobium, and 20-58% nickel, all percentages by weight. Numerous compositions of titanium-niobium-nickel brazing alloys are disclosed.

Zirconia ceramic materials and, particularly, stabilized zirconia ceramic materials, are preferred ceramic materials for many applications. Zirconia ceramics are generally stronger and less reactive in harsh environments than alumina ceramics,
30 making them suitable candidates for applications such as implantable devices. The relative expense of zirconia ceramics and the difficulty of providing reliable hermetic seals at the interface of zirconia ceramics with metallic materials have presented challenges in using zirconia ceramics in many applications. Providing a reliable hermetic seal of zirconia ceramic materials to metallic materials, and particularly
35 titanium-containing metallic materials, has been particularly difficult as a result of the active nature of titanium metals. The methods of the present invention are directed to

- 5 providing reliable, hermetic seals at the interface of ceramic materials, particularly zirconia ceramic materials, with metallic materials, particularly titanium-containing metallic materials.

Summary of the Invention

- 10 The present invention provides methods and braze materials for sealing ceramic materials, such as zirconia materials, to metallic materials, particularly titanium-containing and copper-containing metallic materials, using a braze material comprising titanium and nickel and, optionally, niobium. Broadly, the methods of the present invention may be adapted to seal a variety of ceramic and ceramic-like
- 15 materials, including materials comprising zirconia and stabilized zirconia, alumina, silicon nitride, silicon carbide, titanium carbide, tungsten carbide, titanium nitride, silicon-aluminum oxy-nitride (sialon), graphite, titanium di-boride, boron carbide, zirconia toughened alumina, and molybdenum disilicide. These materials and materials having similar properties are collectively referred to as "ceramic" materials
- 20 in this specification and the appended claims. Zirconia ceramic materials stabilized with yttria, magnesia, ceria, calcia or combinations thereof, are especially preferred ceramic materials.

- Metallic materials to which the ceramic materials may be joined include various titanium-containing, copper-containing, tantalum-containing, and niobium-
- 25 containing materials, including alloys and intermetallic materials, such as titanium-niobium materials and titanium-tantalum materials, as well as niobium, platinum, and other metallic materials, and refractory materials such as molybdenum and zirconium alloys. Titanium-containing, niobium-containing, and copper-containing metallic alloy or intermetallic materials are preferred, with titanium alloys or intermetallics
- 30 such as titanium-niobium, titanium-tantalum and titanium alloys such as 6A14V, composed of 90% titanium, 6% aluminum, and 4% vanadium, are especially preferred. Titanium alloys preferably comprise at least 30% titanium and titanium-niobium alloys preferably comprise at least about 45% titanium and at least about 35% niobium. A titanium-niobium alloy composed of 55% titanium and 45%
- 35 niobium is especially preferred.

5 Braze materials comprising titanium and nickel and, optionally, niobium, may be used according to the present invention, to seal ceramic and metallic components. The seal may be a non-hermetic, mechanical seal. Methods and braze materials of the present invention are particularly well-suited to providing hermetic seals between ceramic and metallic surfaces. Braze materials composed of titanium and nickel
10 comprising at least 35% nickel and at least 35% titanium are preferred for sealing ceramic materials to niobium-containing metallic materials. Braze materials comprising at least about 45% nickel and at least about 45% titanium are more preferred; and braze materials having a 50% titanium and 50% nickel composition are especially preferred for sealing ceramic materials to niobium-containing metallic
15 materials. Braze materials comprising titanium, nickel and niobium and comprising at least 35% titanium, by weight, and at least 15% nickel, by weight, and at least 3% niobium, by weight, are preferred for sealing ceramic materials to metallic materials that do not comprise niobium. Braze materials having at least 45% and, most preferably, 50%, titanium, at least 20% nickel, most preferably 25-35% nickel, and at
20 least 5%, more preferably 5-15% niobium, all weight percentages, are preferred for sealing ceramic materials to metallic surfaces wherein the metallic material does not contain niobium.

Interface surfaces of ceramic and metallic components having various conformations and configurations may be hermetically sealed to one another using
25 braze materials of the present invention. Surfaces to be sealed are cleaned to remove any foreign or oxidized materials and are arranged adjacent and in proximity to one another, with braze material contacting at least one of the interface surfaces in the vicinity of the intended hermetic seal. The braze material is preferably in physical contact with the metallic interface surface. The braze material may be provided as a
30 thin foil member, as a paste comprising metallic powders, as metallic powders or beads, or as a preformed insert (a "preform") having the approximate configuration of the surfaces being sealed and fitting generally between the interface surfaces being sealed. Annular washers comprising braze material may be used, for example, to seal annular or cylindrical interface surfaces.

35 After the braze material is positioned adjacent the interface surfaces to be sealed, the assembly comprising the interface surfaces and braze material is heated

5 under vacuum conditions to the desired sealing temperature for the desired length of time. Sealing temperatures of less than about 1150°C, generally from about 900°C to 1150°C are preferred, with sealing temperatures less than about 1100°C, and preferably from about 1000°C to 1100°C being especially preferred. The braze materials of the present invention are preferably capable of forming a liquidus at a
10 temperature below about 1150°C. For some applications, it is desirable to carry out the brazing process in a substantially inert atmosphere, such as an atmosphere comprising argon or helium gas.

The braze material wets the interface surfaces during the sealing operation, and obviates the need to metalize the ceramic interface surface prior to sealing.
15 Following the formation of a liquidus, the assembly is cooled and a solid, preferably hermetic seal is formed between the interface surfaces. Temperatures may be ramped up to the desired sealing temperature over a predetermined time period and ramped down over a predetermined time period during cooling according to various sealing protocols. For some applications, pressure is applied to the interface surfaces during
20 the sealing process.

Methods and braze materials of the present invention may be used to provide seals on the exterior or interior of an assembly. Multiple components may be sealed simultaneously. According to preferred embodiments, the seals are hermetic. Thus, for example, one or more ceramic to metal assemblies having braze material
25 contacting at least one of the components in the vicinity of the desired seal may be mounted inside a ceramic and metal exterior assembly which, itself, has braze material contacting at least one of the components in the vicinity of the desired seal. The full assembly may be heated to sealing temperatures in a vacuum furnace to produce the desired interior and exterior seals simultaneously.

30 According to preferred embodiments of the present invention, the materials, including the ceramic material, the metallic material, and the braze materials are selected to optimize the sealing operation and the joint formed thereby. In one aspect, this optimization involves the use of a braze material that, in the presence of the metallic surface being sealed, has a melting point lower than it otherwise would. The
35 preferred braze material for use in methods of the present invention for sealing a zirconia ceramic material to a titanium-niobium metallic material, for example, a

5 50-50 titanium-nickel alloy, has a melting point of approximately 1250°C to 1275°C. In the presence of a preferred 55-45 titanium-niobium metallic material and a stabilized zirconia ceramic material, the effective melting point of the 50-50 titanium-nickel sealing alloy is reduced to less than 1150°C, generally to between about 1000°C and 1100°C. Thus, a braze material that may be unsuitable for use with
10 stabilized zirconia ceramic materials as a result of its high melting point, may be used to seal such materials in the presence of selected metallic materials. Under these conditions, the metallic material contributes to the wetting of the ceramic, but does not excessively react and is not degraded during the sealing process.

Methods for sealing ceramic and metallic components of the present invention
15 may be employed for numerous applications. The applications described below include implantable medical devices and electrical connectors. The sealing techniques may be used for many different types of implantable medical devices, artificial joints and structural components, various types of electrical connectors and electronics packages for use in various environments, cutting tool components and inserts, fuel
20 cells, gas sensors, pulp and paper handling equipment, pump components, seawater components, as well as other structural applications, such as golf clubs and other types of sporting goods.

Description of the Figures

25 Preferred embodiments of the present invention will be described with reference to the figures, in which:

Figs. 1A and 1B illustrate schematic cross-sectional top and side views, respectively, of a component assembly comprising a ceramic sleeve component, a braze material preform and a metallic band component aligned prior to heating to
30 form the hermetic ceramic to metal seal;

Fig. 2 illustrates a schematic cross-sectional side view of a hermetically sealed component assembly comprising a metallic pin sealed to a ceramic ferrule which is sealed in a metallic wall, with the ceramic and metallic interface surfaces sealed using a titanium-nickel braze material according to methods of the present invention;

35 Fig. 3 illustrates a schematic cross-sectional side view of a component assembly in which a conductive metallic pin is welded to a metallic disk, which is

5 hermetically sealed to a ceramic washer, with the surface of the ceramic washer sealed to a metallic surface, the ceramic to metallic interface surfaces being sealed according to methods of the present invention;

Fig. 4 illustrates a schematic side view of a component assembly in which a metallic end cap and a metallic sleeve are sealed to opposite interface surfaces of a ceramic component according to sealing methods of the present invention;

10 Fig. 5 illustrates a schematic side view of metallic pins sealed in conical apertures in a ceramic plate;

Fig. 6 illustrates a schematic side view of another component assembly in which a metallic pin is hermetically sealed in an aperture in a ceramic plate; and

15 Figs. 7A and 7B illustrate scanning electron micrographs of a cross-section of a metal (55-45 titanium-niobium) to ceramic (yttria-stabilized zirconia) joint sealed according to methods of the present invention using a 50-50 titanium-nickel braze material, with Fig. 7A showing a 296X magnification, and Fig. 7B showing a 999X magnification.

20

Description of Preferred Embodiments

Methods of the present invention are described below with reference to certain preferred embodiments of component assemblies, such as implantable medical devices and electrical connectors. The methods of the present invention are not limited for use in such applications or in connection with component assemblies having similar configurations or properties. Broadly, the methods of the present invention may be used to provide a seal, preferably a hermetic seal, at the interface surfaces of ceramic components having a variety of geometries and metallic components having a variety of geometries, with the sealed components being used for a variety of applications in diverse environments.

30 Ceramic and ceramic-like materials, such as zirconia, are suitable for use with sealing techniques of the present invention. Ceramic materials comprising zirconia are preferred, and stabilized zirconia materials are especially preferred. Partially stabilized zirconia (PSZ), tetragonal zirconia (TTZ), and zirconia ceramics stabilized with yttria, magnesia, ceria or calcia, or a combination of stabilizing materials, are especially preferred. Suitable materials are available commercially and may be

5 provided in a variety of configurations using, for example, injection molding techniques.

Ceramic materials may be hermetically sealed to various metallic materials using the sealing methods of the present invention. In particular, the sealing methods of the present invention are particularly suitable for sealing zirconia ceramic materials to titanium-containing, copper-containing, and niobium-containing metallic alloys and intermetallic materials and refractory metallic materials such as molybdenum-, zirconium-, tantalum- and niobium-containing metallic materials. Titanium-containing materials, including titanium-niobium and titanium-tantalum are preferred, with titanium-niobium metallic materials comprising at least 45% titanium and 35% niobium being more preferred, and 55-45 titanium-niobium metallic alloys being especially preferred for use with braze materials composed of titanium and nickel. Copper-containing metallic alloys such as chromium-copper, beryllium-copper, and dispersion strengthened copper, as well as titanium alloys containing materials other than niobium, are preferred for use with braze materials comprising titanium, nickel, and niobium. Such materials are particularly suitable for applications involving electrical connectors.

According to one embodiment, braze materials of the present invention comprise titanium-nickel materials comprising at least about 40% titanium and at least about 40% nickel, and most preferably comprise a 50-50 titanium-nickel material. The preferred 50-50 titanium-nickel braze material is available, for example, from WESCO of Belmont, CA. Titanium-nickel braze materials are preferred for sealing ceramic materials to metallic materials comprising niobium. The braze material may be provided in the form of a thin foil having a thickness of about .0001 inch to about .010 inch, with a thickness of about .001 to about .006 inch being preferred, and a thickness of about .003 to about .004 inch being especially preferred. The braze material foil may be arranged at the interface between a ceramic surface and a metallic surface in the vicinity of a desired hermetic seal. Alternatively, the braze material may be provided as a "preform" having the approximate configuration of the desired seal area. Braze material preforms in the configuration of washers may be used, for example, to seal annular and cylindrical components. Annular washers having a 50-50 titanium-nickel composition are especially preferred for use in sealing

5 techniques of the present invention. The braze material may also be provided in the form of metallic beads or powders, or in a paste form in which finely divided powders are combined with a compatible solvent and binder. Suitable solvents and binders are well known in the art.

10 The inventor has discovered that certain combinations of materials interact to provide highly desirable sealing conditions. Specifically, the combination of a 50-50 titanium-nickel braze material to seal the interface surfaces of a ceramic component, such as a stabilized zirconia ceramic component, to a metallic component comprising niobium, more specifically, a metallic component composed of a titanium-niobium
15 metallic alloy and, more specifically, a 55-45 titanium-niobium alloy, is especially preferred. Using these materials, the melting point of the titanium-nickel braze material is effectively lowered so that the sealing operation may be accomplished at temperatures of less than about 1150°C, and generally at temperatures between about 1000°C and 1100°C. These temperatures are well tolerated by the preferred zirconia ceramic materials. Under these conditions, the seal formed by the braze material
20 between the ceramic and metallic interface surfaces is reliable, preferably hermetic, durable and strong. Additionally, the seal area has a unique structure and composition, as described in detail below.

Braze materials comprising titanium, nickel, and niobium are preferred for sealing the interface surfaces of a ceramic component to a metallic component, such
25 as a titanium alloy or intermetallic material, that does not contain niobium. Braze materials suitable for such applications preferably comprise at least 35% titanium and 15% nickel, by weight, and generally comprise at least 3% niobium. Braze materials comprising at least 45% and not more than 80% titanium, at least 15%, and not more than 45% nickel, and at least 2% and not more than 25% niobium, are preferred. Such
30 braze materials form a liquidus at a temperature of less than 1150°C, and preferably less than 1100°C, in the presence of the ceramic and metallic materials being sealed. Exemplary braze materials comprising 70% titanium, 25% nickel, and 5% niobium, and 50% titanium, 35% nickel, and 15% niobium, have been tested and provide hermetic seals between zirconia ceramic and titanium alloy metallic materials.

35 Sealing techniques of the present invention will be described below with reference to specific component assemblies. It will be recognized that the sealing

5 techniques described with reference to the specific components are exemplary only, and that the methods of the present invention may be adapted to provide seals, preferably hermetic seals, at the interface of many different types and configurations of ceramic and metallic components.

10 Figs. 1A and 1B illustrate cross-sectional schematic top and side views of a ceramic sleeve, a braze material preform in the configuration of a washer, and a metallic band component aligned prior to heating to form the hermetic ceramic to metal seal. As shown in Figs. 1A and 1B, ceramic sleeve 10 is in the configuration of a flattened, disk-like sleeve forming an internal cavity 12. Ceramic sleeve 10 has a continuous interface surface 14 for hermetically sealing to metallic band 16. Metallic
15 band 16 has a continuous interface surface 18 that is substantially the same configuration and dimension as interface surface 14 of ceramic sleeve 10. In the embodiment illustrated in Figs. 1A and 1B, interface surfaces 14 and 18 are substantially smooth and flat, and the joint formed between them is referred to as a "butt" joint. It will be recognized that different configurations of interface surfaces
20 may be provided and different types of joints may be sealed using the methods of the present invention.

Metallic band 16 is positioned so that its interface surface 18 is adjacent to interface surface 14 of ceramic sleeve 10. Braze material preform 20 is provided in the form of a washer positioned between the ceramic and metallic interface surfaces
25 14 and 18, respectively. In the preferred embodiment illustrated in Figs. 1A and 1B, braze material preform 20 contacts both ceramic and metallic interface surfaces 14 and 18. According to preferred embodiments, ceramic sleeve 10 is composed stabilized zirconia ceramic material; metallic band 16 is composed of a titanium-niobium alloy and, preferably, a titanium-niobium alloy comprising at least 35%
30 niobium and at least 45% titanium; and braze material preform 20 is composed of a titanium-nickel alloy and, preferably, a 50-50 titanium-nickel alloy preform in the configuration of a washer having a thickness of about .003 to about .004 inch.

The assembly shown in Fig. 1 is heated under vacuum conditions to a sealing temperature of below about 1150°C, preferably to a sealing temperature between
35 about 1000°C and about 1100°C. The desired sealing temperature and times will vary depending upon the composition of the braze material, the configuration and

5 dimensions of the interface surfaces, and the composition of the ceramic and metallic materials being hermetically sealed. For sealing alloys comprising at least 35% titanium and at least 15% nickel in combination with metallic materials comprising at least 45% titanium, the preferred sealing temperature is between about 1000°C and 1100°C, and the sealing time is from several minutes to several hours. The assembly
10 is cooled following heating. The heating and cooling process is preferably accomplished by gradually increasing the temperature from ambient to the desired sealing temperature, and then by gradually reducing the temperature from the desired sealing temperature back to ambient temperatures. The sealing protocol will vary, depending upon the composition of the sealing alloy, the configuration and
15 dimensions of the interface surfaces, and the composition of the materials being sealed.

According to preferred sealing methods using the 50-50 titanium-nickel braze material, the assembly is heated under vacuum conditions from ambient temperature to the desired sealing temperature by increasing the temperature at a predetermined
20 rate until the desired sealing temperature is reached. The assembly is preferably maintained at the sealing temperature for a time period of from about one minute to one hour, preferably about two minutes to about 30 minutes. The assembly is then gradually cooled from the desired sealing temperature to ambient temperature by reducing the temperature at a predetermined rate.

25 Additional configurations of components and assemblies illustrating the sealing techniques and materials of the present invention are illustrated in Figs. 2 – 6. The sealing materials and techniques described above may be employed with these components and assemblies. Fig. 2 illustrates an assembly in which a metallic pin is sealed to an insulating ferrule 24 which, in turn, is sealed in a metallic wall or
30 plate 26. A braze material comprising at least 35% titanium and 15% nickel and, optionally, at least 3% niobium, is employed for each seal. Metallic pin 22 preferably comprises a titanium-containing or niobium-containing, or copper-containing metallic material. Metallic wall or plate 26 similarly preferably comprises a titanium-containing metallic material. Insulating ferrule 24 preferably comprises a ceramic
35 material such as zirconia. For applications in which metallic pin 22 and metallic plate 26 do not contain niobium, niobium is preferably present in the braze material.

5 For the assembly illustrated in Fig. 2, a sealing layer 32 of metallic foil or paste comprising the braze material constituents is positioned between the cylindrical interface surface 28 of metallic pin 22 and the inner cylindrical interface surface 30 of ceramic ferrule 24. Similarly, a sealing layer 34 of metallic foil or paste comprising the braze material constituents is positioned between outer interface surface 36 of
10 ceramic ferrule 24 and interface surface 38 of metallic wall or plate 26. Sealing layer 34 may be co-extensive with the interface surfaces, or may be provided along a portion of the interface surfaces, with the braze material wetting and sealing the length of the interface surface during the sealing process. Sealing, preferably hermetic sealing, of the metallic pin to the ceramic ferrule and the ceramic ferrule to the
15 metallic wall or plate may be accomplished serially or simultaneously.

Using the techniques and components described above, metallic pins having various compositions may be mounted and hermetically sealed in an insulating ferrule which is, in turn, hermetically sealed in a metallic wall or plate. This type of assembly may be used for a variety of applications, including electronics packaging
20 and various types of sensors.

Fig. 3 illustrates an alternative embodiment of a metallic pin mounted in a metallic plate or wall by means of a ceramic element. In this embodiment, metallic pin 40 is mounted in an insulating block 42, which is hermetically sealed to a metallic wall or plate 44 and a metallic plate 58. A braze material comprising at least 35% titanium and 15% nickel and, optionally comprising at least 3% niobium, is provided
25 between the appropriate ceramic and metallic interface surfaces for each seal. Metallic pin 40 preferably comprises a titanium-containing, niobium-containing, or copper-containing metallic material, or another material such as platinum. Metallic wall or plate 44 preferably comprises a titanium-containing, niobium-containing, or copper-containing metallic material. Insulating block 42 preferably comprises a
30 ceramic material such as zirconia.

For the assembly illustrated in Fig. 3, a sealing layer 46 of metallic foil or paste, or a braze material preform comprising the braze material constituents, is positioned between the lower interface surface 48 of insulating block 42 and the
35 interface surface 50 of metallic plate or wall 44. Similarly, a sealing layer 52 of metallic foil or paste, or a preform comprising the braze material constituents, is

5 positioned between upper interface surface 54 of insulating block 42 and a lower interface surface 56 of metallic plate 58. Hermetic sealing of insulating block 42 to metallic wall or plate 44 and metallic plate 58 may be accomplished serially or simultaneously. Metallic pin 40 is hermetically sealed to insulating block 42 by contact with sealing layer 46. Additionally, metallic pin 40 may be hermetically
10 sealed to metallic plate 58 by means of a fusion weld 60, such as electron beam welding or laser welding.

Fig. 4 illustrates yet another application for the sealing materials and methods of the present invention. Annular ceramic element 62 is sealed to metallic sleeve 64 and metallic end cap 66 using the sealing techniques and materials of the present
15 invention. According to a preferred embodiment, a braze material foil or preform 74 comprising titanium and nickel constituents is positioned between oblique ceramic interface surface 70 and corresponding oblique metallic interface surface 72. The conformation and dimensions of braze material foil or preform 74 preferably substantially match the conformation and dimensions of the corresponding interface
20 surfaces. Similarly, braze material foil or preform 76 comprises titanium and nickel constituents and is positioned between ceramic interface surface 78 and metallic interface surface 80. The assembly is heated under vacuum conditions to the desired sealing temperature and cooled to hermetically seal ceramic element 62 to the metallic end cap and sleeve simultaneously.

25 Fig. 5 illustrates yet another configuration of ceramic and metallic members and interface surfaces that are hermetically sealed using the techniques and materials of the present invention. In the embodiment of Fig. 5, frustoconical metallic pin or plug 82 is hermetically sealed in a recess 84 in ceramic plate 86 having a corresponding configuration and dimension using braze material preform 88. Fig. 6
30 illustrates a component assembly in which metallic pin 90 is mounted through metallic washer 96 and recess 92 in ceramic plate 94. Braze material preform 98 comprising titanium and nickel metals is placed between the interface surfaces of metallic washer 96 and ceramic plate 94, and the assembly is heated under vacuum conditions to sealing temperatures. During the sealing process, the braze material
35 forms a liquidus which wets and seals the interface surfaces between metallic washer 96 and ceramic plate 94. The braze material also wets the interface surfaces between

5 metallic pin 90 and recess 92 of ceramic plate 94 and forms a hermetic seal at those interface surfaces as well. The dimensions and volume of braze material preform 98 may be adjusted to provide braze material sufficient to wet and seal the desired interface surfaces during heating and cooling. This component configuration may be used, for example, in connection with electronics packages and implantable medical
10 devices.

For some applications, sealing methods of the present invention involve the application of pressure to one or more of the interface surfaces in the direction of the joint during heating and cooling. Thus, for example, pressure may be exerted on the ceramic sleeve and/or the metallic band illustrated in Figs. 1A and 1B during heating
15 to press or squeeze interface surfaces 14 and 18 toward one another. Application of pressures on the order of from about 2,000 to 5,000 psi, preferably about 3,500 to 4,500 psi, and most preferably about 4,000 psi is suitable. For sealing applications such as those illustrated in Figs. 4-6, application of pressure to the "top" of the assembly during sealing, such as by use of a weight, is preferred. Ramping of the
20 application of pressure so that the pressure increases as the temperature increases and the pressure is of the desired maximum when the sealing temperature is attained may be desirable for some sealing applications.

The sealing process of the present invention, when employed in connection with preferred braze materials comprising at least 35% titanium and at least 15%
25 nickel and preferred metallic materials comprising titanium and/or niobium, effectively lowers the melting point of the sealing alloy. One preferred braze material, composed of a 50-50 titanium-nickel alloy, has a melting point of about 1250°C to about 1275°C. Using the materials and methods of the present invention, the preferred 50-50 titanium-nickel sealing alloy forms a liquidus at temperatures less
30 than about 1150°C, and preferably between about 1000°C and 1100°C. The desired lowering of the temperature at which the sealing alloy forms a liquidus occurs in the presence of a metallic material comprising titanium and/or niobium.

Figs. 7A and 7B illustrate 296X and 999X scanning electron micrographs, respectively, of a cross section of a joint sealed according to methods of the present
35 invention. Zone A is a titanium-niobium metallic component comprising a 55-45 titanium-niobium alloy; zone B is the interface area and incorporates a braze material

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- 5 comprising a 50-50 titanium-nickel; and zone C is a yttria-stabilized zirconia material. The titanium-niobium metallic component was sealed to the zirconia component using the 50-50 titanium-nickel braze material using the methods described above.

Elemental compositions of various regions indicated at flags 1-7 and 9-11 of the joint and surrounding material were determined using energy dispersive x-ray analysis. The results were as follows:

| Flag | Elemental Composition |
|------|---|
| 1 | Preponderance of titanium and niobium in proportion to the bulk 55-45 composition of the metallic material with a small amount of nickel. |
| 2 | Preponderance of titanium and niobium, with a smaller niobium peak than at flag 1, and a larger amount of nickel than at flag 1. |
| 3 | Preponderance of titanium, with a sizeable nickel peak and a small niobium peak. |
| 4 | Preponderance of titanium, with a sizeable nickel peak and a small niobium peak – very similar to the composition at flag 3. |
| 5 | Preponderance of titanium, with a sizeable nickel peak and a small niobium peak – very similar to the composition at flags 3 and 4. |
| 6 | Preponderance of titanium and niobium in nearly equal amounts and a very small amount of nickel. |
| 7 | Preponderance of titanium, with a substantial niobium peak, a less substantial nickel peak, and a small zirconium peak. |
| 9 | Preponderance of titanium with small nickel, niobium and zirconium peaks. |
| 10 | Preponderance of titanium with small niobium and nickel peaks and a larger zirconium peak. |
| 11 | Preponderance of zirconium with a small yttria peak and very small titanium peaks. |

- The analytical results demonstrate that, during the sealing process, there is significant migration of elements between the metallic material and the braze material.
- 15 Significant amounts of nickel were identified at flags 1-3, in the titanium-niobium metallic material, and at the interface between the titanium-niobium metallic material and the titanium-nickel sealing alloy. Nickel from the sealing material thus migrates into the metallic material. The interface area designated generally as zone B, which incorporates the braze material layer, has a large number of dispersed granular
- 20 structures. The analysis of interface zone B at flags 4 and 5, which does not evidence a granular structure, indicates the presence of titanium and nickel, with a small

5 amount of niobium. The analysis at flag 6, which is within a granular structure in interface zone B, indicates a preponderance of niobium and titanium, with only a small amount of nickel. The interface zone of the joint, in the area of the sealing alloy, is thus characterized by granular structures having a high niobium content. Niobium from the metallic material migrates into the sealing alloy in the interface
10 zone and forms high niobium content granules during the sealing process.

A hermetically sealed assembly of the present invention may include a metallic material comprising titanium and/or niobium, an interface zone in the area of a braze material comprising titanium, nickel, and optionally, niobium, and a ceramic material. The assembly of the present invention is characterized by the presence of
15 granular structures in the interface zone, as shown, for example, in scanning electron micrographs of a cross section of the joint area. The granular structures have a composition different from that of the braze material. Specifically, when the metallic material of the assembly comprises titanium and niobium, granular structures present in the interface zone have a high niobium content and, generally, the granular
20 structures present in the interface zone largely comprise niobium and titanium. According to preferred embodiments, using energy dispersive x-ray analysis, granular structures present in the interface zone demonstrate a niobium peak that is at least 50% as large as the titanium peak and, in especially preferred embodiments, the titanium and niobium peaks are generally equivalent. Assemblies incorporating
25 ceramic to metal seals made according to the sealing methodology of the present invention may be identified based on the presence of high niobium content granules in the interface zone.

While the sealing methods, braze materials, and sealed assemblies of the present invention have been described with respect to certain preferred embodiments
30 thereof and many details have been set forth for purposes of describing the invention in detail, it will be recognized that additional configurations, embodiments and materials may be used without departing from the invention.

5 I Claim:

1. A method for sealing an interface surface of a ceramic material to an interface surface of a metallic material comprising:

10 positioning the interface surface of the ceramic material and the interface surface of the metallic material in proximity to one another and contacting at least one of the interface surfaces with a titanium-containing braze material comprising at least about 15% nickel;

15 heating the braze material under vacuum conditions to a temperature of less than about 1150°C and melting the braze material to form a liquidus contacting both the interface surface of the ceramic material and the interface surface of the metallic material;

cooling the braze material, thereby forming a solid seal between the interface surface of the ceramic material and the interface surface of the metallic material.

20 2. The method of claim 1, wherein the ceramic material comprises a material selected from the group consisting of: zirconia, alumina, silicon nitride, silicon carbide, titanium carbide, tungsten carbide, titanium nitride, silicon-aluminum oxynitride, graphite, titanium di-boride, boron carbide, and molybdenum disilicide.

25 3. The method of claim 2, wherein the ceramic material comprises zirconia.

4. The method of claim 3, wherein the ceramic material comprises zirconia stabilized with a material selected from the group consisting of: yttria; ceria; calcia; magnesia; or combinations thereof.

30

5. The method of claim 1, wherein the metallic material is a titanium-containing alloy or intermetallic material.

35 6. The method of claim 5, wherein the metallic material is a titanium-niobium alloy.

5

7. The method of claim 6, wherein the metallic material is a titanium-niobium alloy comprising at least about 45% titanium.

8. The method of claim 6, wherein the metallic material is a titanium-niobium alloy comprising at least about 35% niobium.

9. The method of claim 6, wherein the metallic material is a 55-45 titanium-niobium alloy.

10. The method of claim 1, wherein the metallic material is a copper-containing alloy.

11. The method of claim 10, wherein the metallic material comprises a material selected from the group consisting of: chromium-copper, beryllium-copper, and dispersion strengthened copper.

12. The method of claim 1, wherein the metallic material is niobium or a niobium-containing alloy or intermetallic material.

13. The method of claim 1, comprising heating the braze material to a temperature of from 1000 to 1100°C.

14. The method of claim 13, comprising gradually heating the braze material to a temperature of from 1000 to 1100°C, maintaining the temperature of 1000 to 1100°C for about two to thirty minutes, and then gradually cooling the braze material.

15. The method of claim 1, additionally comprising applying pressure to at least one of the interface surfaces during heating of the braze material.

- 5 16. The method of claim 14, comprising applying pressure of from about 2,000 psi to about 5,000 psi to at least one of the interface surfaces during heating of the braze material.
- 10 17. The method of claim 1, wherein the braze material comprises at least 35% titanium.
18. The method of claim 17, wherein the braze material is a 50-50 titanium-nickel material.
- 15 19. The method of claim 1, wherein the braze material additionally comprises niobium.
- 20 20. The method of claim 19, wherein the braze material comprises at least 3% niobium.
21. An insert adapted for contacting two adjacent interface surfaces having an annular configuration and composed of a braze material comprising at least 35% titanium and at least 15% nickel.
- 25 22. A component assembly composed of at least two adjacent interface surfaces, comprising: a metallic component having a interface surface comprising a material selected from the group consisting of: a titanium-containing material, a niobium-containing material, a platinum-containing material, a copper-containing material, or a refractory metallic material, the metallic component in contact with a braze material
- 30 comprising at least 35% titanium and at least 15% nickel, the braze material being capable of forming a liquidus at a temperature of less than about 1150°C, the braze material additionally in contact with an interface surface of a ceramic component.
23. A component assembly according to claim 22, wherein the braze material
- 35 additionally comprises at least 3% niobium.

5 24. A component assembly according to claim 22, wherein the braze material comprises a 50-50 titanium-nickel material.

25. A component assembly according to claim 22, wherein the interface surface of the ceramic component comprises a material selected from the group consisting of:
10 zirconia; alumina; silicon nitride; silicon carbide; titanium carbide; tungsten carbide; titanium-nitride; silicon-aluminum oxy-nitride; graphite; titanium di-boride; boron carbide; and molybdenum disilicide.

26. A component assembly comprising a metallic component and a ceramic
15 component, wherein an interface surface of the metallic component is hermetically sealed to an adjacent interface surface of the ceramic component by means of an intermediate layer of a metallic material comprising at least about 35% nickel and having a melting point, in the presence of the interface surface of the metallic component, of less than about 1150°C.

20

27. A component assembly according to claim 26, wherein the intermediate layer of metallic material comprises a 50-50 titanium-nickel alloy.

28. A component assembly according to claim 26, wherein the metallic
25 component comprises a titanium-niobium alloy and the ceramic component comprises zirconia.

29. An assembly comprising a metallic component and a ceramic component, wherein an interface surface of the metallic component is hermetically sealed to an
30 adjacent interface surface of the ceramic component, the assembly having an interface zone comprising a braze material and the interface zone having a plurality of granular structures dispersed in the sealing alloy material.

30. An assembly according to claim 29, wherein the metallic component
35 comprises a titanium-containing material, the ceramic component comprises a

- 5 zirconia ceramic, the braze material is a titanium-containing material, and the granular structures have a high niobium content.

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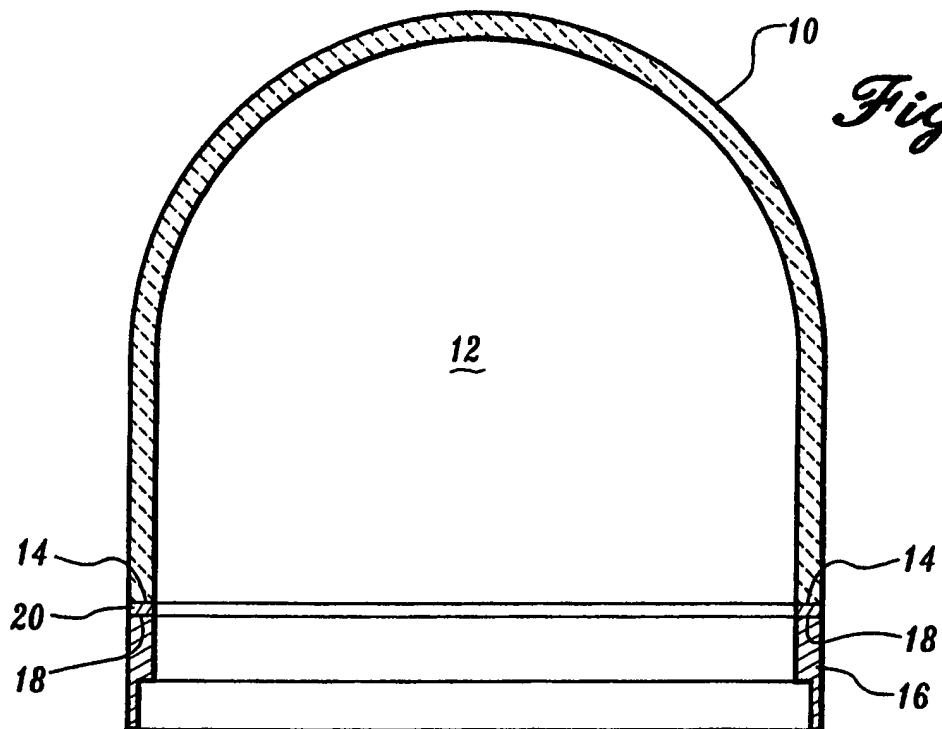


Fig. 1A

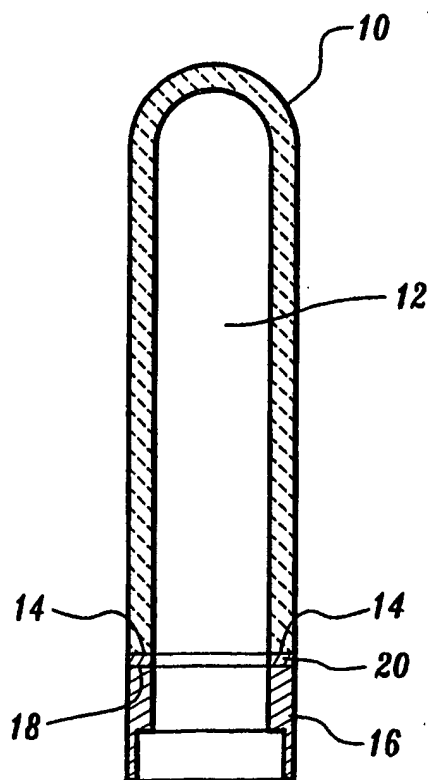


Fig. 1B

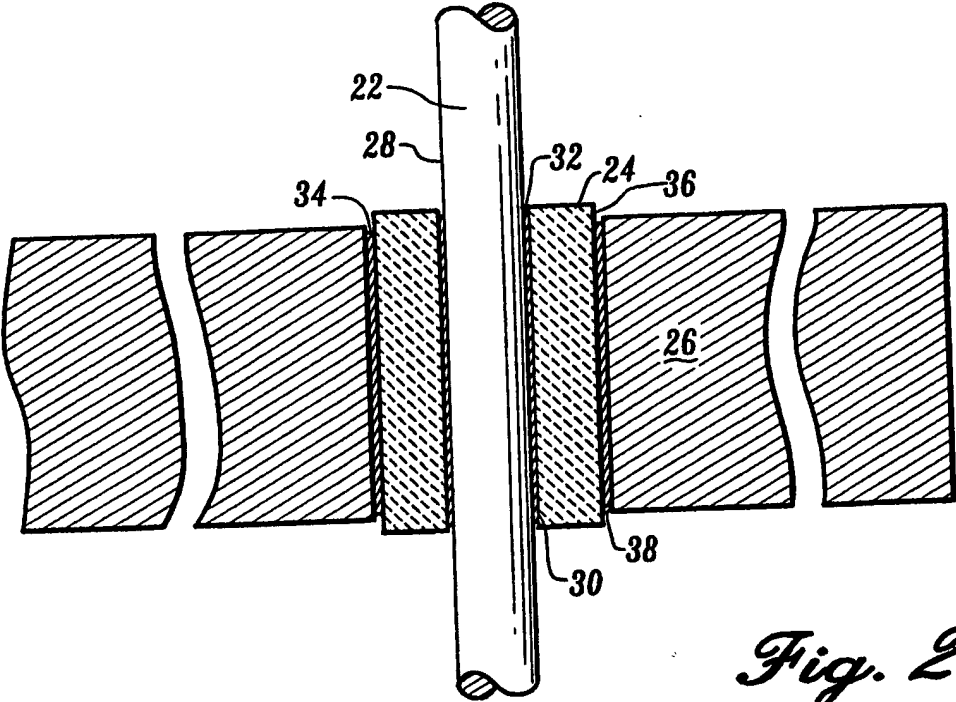


Fig. 2

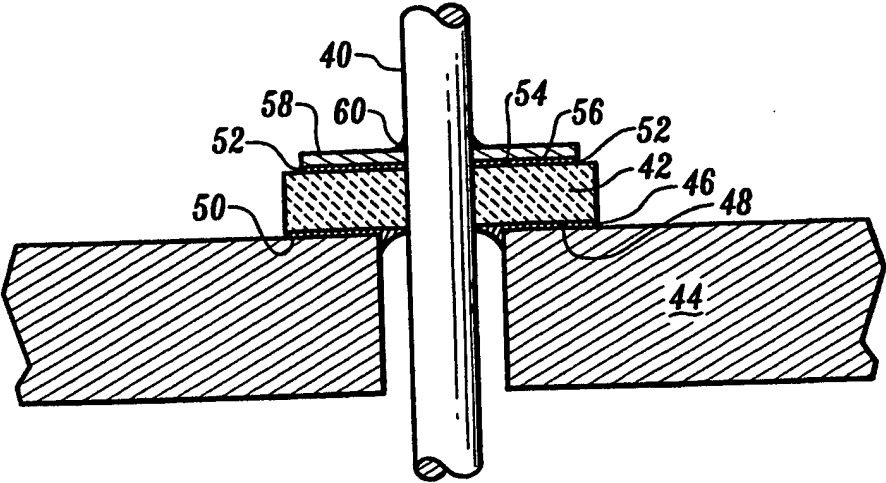
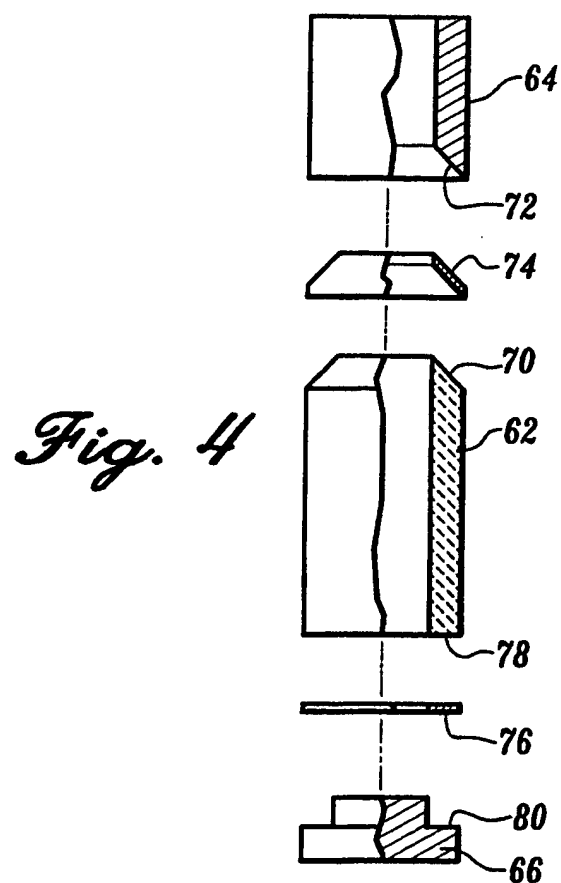


Fig. 3

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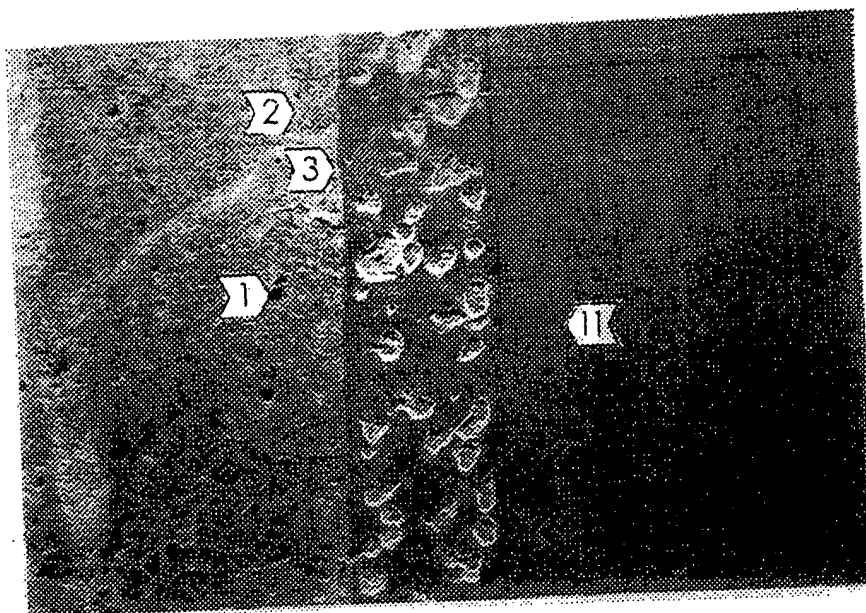


Fig. 7A

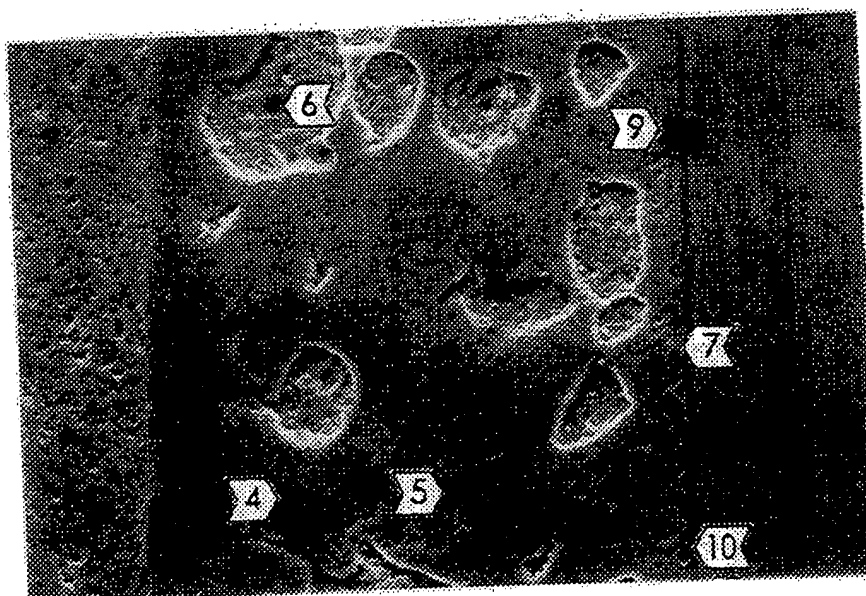


Fig. 7B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/10313

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---------------|--|---|
| X --- Y | JP 8-067575 A (HIRAI ET AL.) 12 March 1996, Abstract; and column 1, line 1 through column 4, line 27. | 1, 2, 13-15, 17, 26, 29 ----- 5-12, 16, 18, 21, 22, 24, 25, 27 |
| X --- Y | JP 4-187573 A (KAMISHINO ET AL.) 06 July 1992, Abstract; Tables; and pages 4-8. | 1, 2, 13-15, 17, 26, 29 ----- 5-12, 16, 18, 21, 22, 24, 25, 27 |
| X --- Y | US 3,662,455 A (ANDERSON) 16 May 1972, column 1, line 55 through column 2, line 73; and Claims 1-16. | 1, 2, 12-15, 17-20, 22-27, 29 ----- 3-11, 16, 21, 28, 30 |
| Y | US 5,334,344 A (HEGNER ET AL.) 02 August 1994, Abstract; column 1, lines 10-19; column 1, line 55 through column 3, line 21; column 3, line 46 through column 5, line 5; and Claims 1-3. | 1-30 |
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| X --- Y | US 3,594,895 A (HILL ET AL.) 27 July 1971, Abstract; column 1, line 55 through column 3, line 12; and Claims 1-8. | 1-4, 13-15, 17, 18, 24, 26, 27, 29 ----- 5-12, 16, 21, 22, 25, 28, 30 |

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/10313

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B32B 15/04; C03C 27/04; C22C 14/00, 27/02, 19/03

US CL :428/660; 420/417; 148/421, 669

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/660, 668, 662, 678, 679, 632, 633, 627; 420/417, 426, 441; 148/421, 422, 426, 668, 669, 670, 671, 675, 677, 676

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---------------|---|--|
| Y | US 3,309,767 A (SAMA ET AL.) 21 March 1967, column 1, line 36 through column 2, line 59; and claims 1-3. | 1-30 |
| X --- Y | US 3,091,028 A (WESTBROOK ET AL.) 28 May 1963, column 2, line 24 through column 4, line 13; and Claims 1-9. | 1-4, 13-15, 18, 26, 27, 29 5-12, 16, 17, 21, 22, 24, 25, 28, 30 |



Further documents are listed in the continuation of Box C.



See patent family annex.

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| *P* document published prior to the international filing date but later than the priority date claimed | |

Date of the actual completion of the international search

11 JUNE 1999

Date of mailing of the international search report

07 JUL 1999

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